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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

00850137.1

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

I.L.C. HATTEN-HECKMAN

DEN HAAG, DEN
THE HAGUE, 10/07/01
LA HAYE, LE



**Blatt 2 der Bescheinigung
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Page 2 de l'attestation**

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Sizing dispersion

The present invention refers to an aqueous dispersion of a sizing agent comprising a cationic or amphoteric organic polymer containing at least one aromatic group.

5 Background

Aqueous dispersions or emulsions of sizing agents are used in papermaking in order to give paper and paper board improved resistance to wetting and penetration by various liquids.

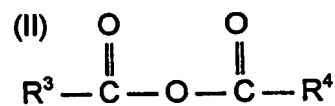
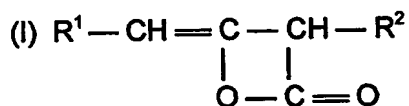
10 Dispersions of sizing agents generally contain an aqueous phase and finely divided particles or droplets of the sizing agent dispersed therein. The dispersions are usually prepared by homogenizing the sizing agent, water insoluble material in an aqueous phase in the presence of a dispersant using high shear forces and fairly high temperatures. Dispersants conventionally used include anionic, amphoteric and cationic high molecular weight polymers, e.g. lignosulfonates, starches, polyamines, polyamideamines, and vinyl
15 addition polymers. The polymers can be used singly, together or in combination with other compounds to form a dispersant system. Depending on the overall charge of the components of the dispersant system, the size dispersions will be anionic or cationic in nature. The sizing dispersions are usually added to an aqueous suspension containing cellulosic fibres, optional fillers and various additives.

20 The cellulosic suspension contains a certain amount of non-fibrous material, for example fillers, colloidal substances, charged polymers and various charged contaminants, i.e. anionic trash, electrolytes, charged polymers etc.. The charged contaminants has an influence on the sizing efficiency and commonly impairs the sizing performance. High amounts of charged contaminants such as high contents of salts in
25 the suspension renders a suspension which is increasingly difficult to size, i.e. to obtain a paper with satisfactory sizing properties. Other compounds contained in the suspension which deteriorates sizing are various lipophilic wood extractives which may come from recycled fibres and mechanical pulps. An increased amount of added sizing agent often improve sizing, however, leading to higher costs as well an increased accumulation of
30 sizing agents in the white water. The accumulation of non-fibrous material as well as any other components present in the suspension will be even more pronounced in mills where white water is extensively recirculated with the introduction of only low amounts of fresh water into the papermaking process. Thus, it is an objective of the present invention to further improve sizing. Another objective of the present invention is to improve sizing
35 when applying sizes on cellulosic suspensions having high conductivities. Still another objective of the present invention is that the stability of the dispersions are improved. Yet further objectives will appear hereinafter.

Invention

In accordance with the invention it has been surprisingly been found that improved sizing can be obtained with an aqueous dispersion according to the claims. More specifically, the present invention refers to an aqueous dispersion of a sizing agent comprising a cationic or amphoteric organic polymer, wherein the organic polymer contains at least one aromatic group. The present invention further also encompasses a method for the preparation of an aqueous dispersion as well the use of the dispersion as a stock size and surface size.

The sizing agent of the dispersion according to the present invention is suitably any sizing agent known, such as non-cellulose-reactive agents including rosin, i.e. disproportionated rosin, hydrogenated rosin, polymerized rosin, formaldehyde-treated rosin, esterified rosin, fortified rosin and mixtures of such treatments and so treated rosins, fatty acids and derivatives thereof, e.g. fatty acid esters and amides like bis-stearamide, resin and derivatives thereof, e.g. hydrocarbon resins, resin acids, resin acid esters and amides, waxes, e.g. crude and refined paraffin waxes, synthetic waxes, naturally occurring waxes, etc. and/or cellulose-reactive agents. Preferably, the sizing agent is a cellulose-reactive sizing agent. The cellulose-reactive sizing agents comprised in the sizing dispersion can be selected from any cellulose-reactive agents known in the art. Suitably, the sizing agent is selected from the group consisting of hydrophobic ketene dimers, ketene multimers, acid anhydrides, organic isocyanates, carbamoyl chlorides and mixtures thereof, preferably ketene dimers and acid anhydrides, most preferably ketene dimers. Suitable ketene dimers have the general formula (I) below, wherein R^1 and R^2 represent saturated or unsaturated hydrocarbon groups, usually saturated hydrocarbons, the hydrocarbon groups suitably having from 8 to 36 carbon atoms, usually being straight or branched chain alkyl groups having 12 to 20 carbon atoms, such as hexadecyl and octadecyl groups. In a preferred embodiment the ketene dimers are liquid at ambient temperature, i.e. at 25 °C, suitably at 20 °C. Suitable acid anhydrides can be characterized by the general formula (II) below, wherein R^3 and R^4 can be identical or different and represent saturated or unsaturated hydrocarbon groups suitably containing from 8 to 30 carbon atoms, or R^3 and R^4 together with the -C-O-C- moiety can form a 5 to 6 membered ring, optionally being further substituted with hydrocarbon groups containing up to 30 carbon atoms. Examples of acid anhydrides which are used commercially include alkyl and alkenyl succinic anhydrides and particularly isooctadecenyl succinic anhydride.



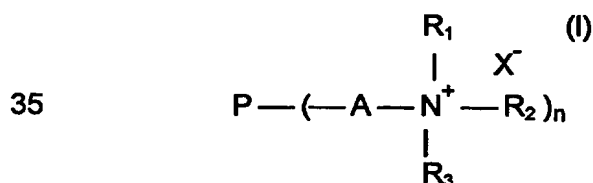
Suitable ketene dimers, acid anhydrides and organic isocyanates include the compounds disclosed in U.S. Pat. No. 4,522,686, which is hereby incorporated herein by reference. Examples of suitable carbamoyl chlorides include those disclosed in U.S. Pat. No. 3,887,427 which is also incorporated herein by reference.

Aqueous dispersions according to the present invention comprise a cationic or amphoteric organic polymer containing at least one aromatic group. Suitably, the organic polymer is a cationic or amphoteric polysaccharide containing at least one aromatic group or a cationic organic synthetic polymer containing at least one aromatic group.

Cationic or amphoteric polysaccharides according to the invention suitably has at least one aromatic group and at least one cationic group, the cationic group suitably being tertiary amino groups or, preferably, quaternary ammonium groups. The polysaccharide may also contain one or more anionic groups which can be, for example, phosphate, phosphonate, sulphate, sulphonate or carboxylic acid groups and they are preferably phosphate groups. If present, the anionic groups can be native or introduced by means of chemical treatment in conventional manner; native potato starch contains a substantial amount of covalently bound phosphate monoester groups. In amphoteric polysaccharides, cationic groups are preferably present in a predominant amount.

The aromatic group of the polysaccharide can be attached to a heteroatom like oxygen present in the polysaccharide. Preferably, the aromatic group is attached to a heteroatom, e.g. nitrogen or oxygen, the heteroatom optionally being charged, for example when it is a nitrogen. The aromatic group can also be attached to a group comprising a heteroatom, e.g. amide, ester or ether, which groups can be attached to the polysaccharide backbone(main-chain), for example via a chain of atoms. Example of suitable aromatic groups and groups comprising an aromatic group include aryl and aralkyl groups, e.g. phenyl, phenylene, naphthyl, phenylene, xylylene, benzyl and phenylethyl; nitrogen-containing aromatic (aryl) groups, e.g. pyridinium and quinolinium, as well as derivatives of these groups where one or more substituents attached to said aromatic groups can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

Particularly suitable polysaccharides comprised in the sizing dispersion and/or comprised in the sizing promoter include those comprising the general structural formula (I):



wherein P is a residue of a polysaccharide; A is a group attaching N to the polysaccharide residue, suitably a chain of atoms comprising C and H atoms, and optionally O and/or N atoms, usually an alkylene group with from 2 to 18 and suitably 2 to 8 carbon atoms, optionally interrupted or substituted by one or more heteroatoms, e.g. O or N, e.g. an
 5 alkyleneoxy group or hydroxy propylene group ($\text{—CH}_2\text{—CH(OH)—CH}_2\text{—}$); R_1 and R_2 are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, suitably 1 or 2 carbon atoms; R_3 is an aromatic hydrocarbon group including aralkyl groups, e.g. benzyl and phenylethyl groups; n is an integer from about 2 to about 300,000, suitably from 5 to 200,000 and preferably from 6 to 125,000 or, alternatively, R_1 ,
 10 R_2 and R_3 together with N form a aromatic group containing from 5 to 12 carbon atoms; and X^- is an anionic counterion, usually a halide like chloride.

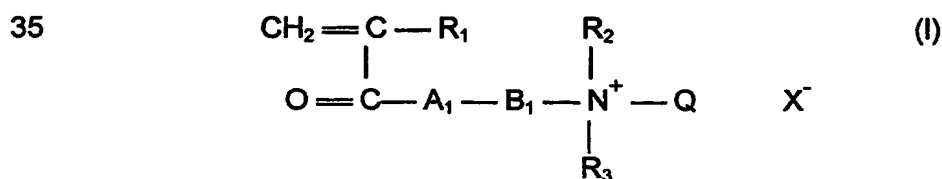
The aromatic group modified cationic or amphoteric polysaccharide can have a degree of substitution varying over a wide range; the degree of cationic substitution (DS_C) can be from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, the degree of
 15 aromatic substitution (DS_H) can be from from 0,01 to 0,5, suitably from 0,02 to 0,3, preferably from 0,025 to 0,2, and the degree of anionic substitution (DS_A) can be from 0 to 0,2, suitably from 0 to 0,1, preferably from 0 to 0,05.

The polysaccharides can be prepared by subjecting a polysaccharide to cationic and aromatic modification in known manner using one or more agents containing a cationic
 20 group and/or a aromatic group, for example by reacting the agent with the polysaccharide in the presence of an alkaline substance such as an alkali metal or alkaline earth metal hydroxide. The polysaccharide to be subjected to cationic and aromatic modification can be non-ionic, anionic, amphoteric or cationic. Suitable modifying agents include non-ionic agents such as, for example, aromatic substituted succinic anhydrides; aralkyl halides, e.g.
 25 benzyl chloride and benzyl bromide; the reaction products of epichlorohydrin and dialkylamines having at least one substituent comprising an aromatic group as defined above, including 3-dialkylamino-1,2-epoxypropanes; and cationic agents such as, for example, the reaction product of epichlorohydrin and tertiary amines having at least one substituent comprising an aromatic group as defined above, including trialkylamines,
 30 alkaryldialkylamines, e.g. dimethylbenzylamine; arylamines, e.g. pyridine and quinoline. Suitable cationic agents of this type include 2,3-epoxypropyl trialkylammonium halides and halohydroxypropyl trialkylammonium halides, e.g. N-(3-chloro-2-hydroxypropyl)-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride and N-glycidyl-N-(hydrophobic alkyl)-N,N-di(lower alkyl)ammonium chloride where the aromatic group is as defined above,
 35 notably octyl, decyl and dodecyl, and the lower alkyl is methyl or ethyl; and halohydroxypropyl-N,N-dialkyl-N-alkarylammonium halides and N-glycidyl-N-(alkaryl)-N,N-dialkylammonium chloride, e.g. N-(3-chloro-2-hydroxypropyl)-N-(alkaryl)-N,N-di(lower alkyl)-

ammonium chloride where the alkaryl and lower alkyl groups are as defined above, particularly N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride; and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Generally, when using a non-ionic aromatic agent, the polysaccharide is suitably rendered cationic by using any of the cationic agents known in the art before or after the hydrophobic modification. Examples of suitable cationic and/or aromatic modifying agents, aromatic group modified polysaccharides and methods for their preparation include those described in U.S. Patent Nos. 4,687,519 and 5,463,127; International Patent Application WO 94/24169, European Patent Application No. 189 935; and S.P. Patel, R.G. Patel and V.S. Patel, Starch/Stärke, 41(1989), No. 5, pp. 192-196, the teachings of which are hereby incorporated herein by reference.

Cationic organic synthetic polymers containing at least one aromatic group according to the invention can be linear or branched and preferably is water soluble or water-dispersable. The aromatic group of the cationic organic synthetic polymer can be present in the polymer backbone or, preferably, it can be a pendent group attached to or extending from the polymer backbone or be present in a pendent group that is attached to or extending from the polymer backbone (main chain). Suitable aromatic (aryl) groups include those comprising a phenyl group, optionally substituted, a phenylene group, optionally substituted, and a naphthyl group, optionally substituted, for example groups having the general formulae $-C_6H_5$, $-C_6H_4-$, $-C_6H_3-$, and $-C_6H_2-$, e.g. in the form of phenylene ($-C_6H_4-$), xylylene ($-CH_2-C_6H_4-CH_2-$), phenyl ($-C_6H_5$), benzyl ($-CH_2-C_6H_5$), phenethyl ($-CH_2CH_2-C_6H_5$), and substituted phenyl (for example $-C_6H_4-Y$, $-C_6H_3Y_2$, and $-C_6H_2Y_3$) where one or more substituents (Y) attached to the phenyl ring can be selected from hydroxyl, halides, e.g. chloride, nitro, and hydrocarbon groups having from 1 to 4 carbon atoms.

The cationic organic synthetic polymer can be selected from homopolymers and copolymers prepared from one or more monomers comprising at least one monomer having an aromatic group, suitably an ethylenically unsaturated monomer, and the cationic organic polymer is suitably a vinyl addition polymer. The term "vinyl addition polymer", as used herein, refers to a polymer prepared by addition polymerization of one or more vinyl monomers or ethylenically unsaturated monomers which include, for example, acrylamide-based and acrylate-based monomers. Suitable cationic organic synthetic polymers include cationic vinyl addition polymers obtained by polymerizing a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (I):



wherein R_1 is H or CH_3 ; R_2 and R_3 are each or, preferably, an alkyl group having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_1 is O or NH; B_1 is an alkylene group having from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group;

5 Q is a substituent containing an aromatic group, suitably a phenyl or substituted phenyl group, which can be attached to the nitrogen by means of an alkylene group usually having from 1 to 3 carbon atoms, suitably 1 to 2 carbon atoms, and preferably Q is a benzyl group ($-CH_2-C_6H_5$); and X^- is an anionic counterion, usually a halide like chloride. Examples of

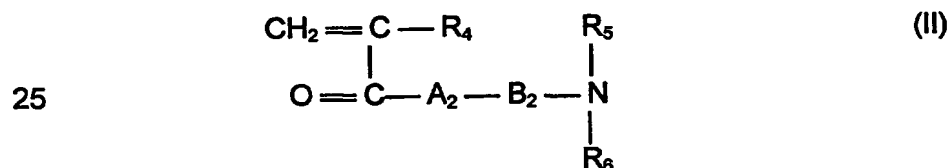
suitable monomers represented by the general formula (I) include quaternary monomers

10 obtained by treating dialkylaminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl (meth)acrylate, and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide, and diethylaminopropyl (meth)acrylamide, with benzyl chloride. Preferred cationic monomers of the general

15 formula (I) include dimethylaminoethylacrylate benzyl chloride quaternary salt and dimethylaminoethylmethacrylate benzyl chloride quaternary salt.

The cationic organic synthetic polymer can be a homopolymer prepared from a cationic monomer having an aromatic group or a copolymer prepared from a monomer mixture comprising a cationic monomer having an aromatic group and one or more

20 copolymerizable monomers. Suitable copolymerizable non-ionic monomers include monomers represented by the general formula (II):



wherein R_4 is H or CH_3 ; R_5 and R_6 are each H or a hydrocarbon group, suitably alkyl, having

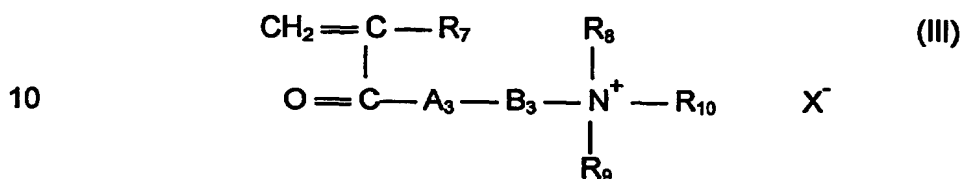
30 from 1 to 6, suitably from 1 to 4 and usually from 1 to 2 carbon atoms; A_2 is O or NH; B_2 is an alkylene group of from 2 to 8 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group or, alternatively, A and B are both nothing whereby there is a single bond between C and N ($O=C-NR_5R_6$). Examples of suitable copolymerizable monomers of this type include (meth)acrylamide; acrylamide-based monomers like N-alkyl

35 (meth)acrylamides and N,N-dialkyl (meth)acrylamides, e.g. N-n-propylacrylamide, N-isopropyl (meth)acrylamide, N-n-butyl (meth)acrylamide, N-isobutyl (meth)acrylamide and N-t-butyl (meth)acrylamide; and dialkylaminoalkyl (meth)acrylamides, e.g. dimethylaminoethyl (meth)acrylamide, diethylaminoethyl (meth)acrylamide, dimethylaminopropyl (meth)acrylamide and diethylaminopropyl (meth)acrylamide; acrylate-based monomers like dialkyl-

40 aminoalkyl (meth)acrylates, e.g. dimethylaminoethyl (meth)acrylate, diethylaminoethyl

(meth)acrylate, t-butylaminoethyl (meth)acrylate and dimethylaminohydroxypropyl acrylate; and vinylamides, e.g. N-vinylformamide and N-vinylacetamide. Preferred copolymerizable non-ionic monomers include acrylamide and methacrylamide, i.e. (meth)acrylamide, and the main polymer is preferably an acrylamide-based polymer.

- 5 Suitable copolymerizable cationic monomers include the monomers represented by the general formula (III):



- wherein R_7 is H or CH_3 ; R_8 , R_9 and R_{10} are each H or, preferably, a hydrocarbon group, suitably alkyl, having from 1 to 3 carbon atoms, usually 1 to 2 carbon atoms; A_3 is O or NH; B_3 is an alkylene group of from 2 to 4 carbon atoms, suitably from 2 to 4 carbon atoms, or a hydroxy propylene group, and X^- is an anionic counterion, usually methylsulphate or a halide like chloride. Examples of suitable cationic copolymerizable monomers include acid addition salts and quaternary ammonium salts of the dialkylaminoalkyl (meth)acrylates and dialkylaminoalkyl (meth)acrylamides mentioned above, usually prepared using acids like HCl, H_2SO_4 , etc., or quaternizing agents like methyl chloride, dimethyl sulphate, etc.; and diallyldimethylammonium chloride. Preferred copolymerizable cationic monomers include dimethylaminoethyl (meth)acrylate methyl chloride quaternary salt and diallyldimethylammonium chloride. Copolymerizable anionic monomers like acrylic acid, methacrylic acid, various sulfonated vinyl addition monomers, etc. can also be employed and, preferably, in minor amounts.
- 15
- 20
- 25

- The cationic organic synthetic polymer can be prepared from a monomer mixture generally comprising from 1 to 99 mole%, suitably from 2 to 50 mole% and preferably from 5 to 20 mole% of cationic monomer having an aromatic group, preferably represented by the general formula (I), and from 99 to 1 mole%, suitably from 98 to 50 mole%, and preferably from 95 to 80 mole% of other copolymerizable monomers which preferably comprises acrylamide or methacrylamide ((meth)acrylamide), the monomer mixture suitably comprising from 98 to 50 mole% and preferably from 95 to 80 mole% of (meth)acrylamide, the sum of percentages being 100.
- 30

- 35 The cationic organic synthetic polymer can also be selected from polymers prepared by condensation reaction of one or more monomers containing an aromatic group. Examples of such monomers include toluene diisocyanates, bisphenol A, phthalic acid, phthalic anhydride, etc., which can be used in the preparation of cationic polyurethanes, cationic polyamideamines, etc.

Alternatively, or additionally, the cationic organic synthetic polymer can be a polymer subjected to aromatic modification using an agent containing an aromatic group. Suitable modifying agents of this type include benzyl chloride, benzyl bromide, N-(3-chloro-2-hydroxypropyl)-N-benzyl-N,N-dimethylammonium chloride, and N-(3-chloro-2-hydroxypropyl) pyridinium chloride. Suitable polymers for such an aromatic modification include vinyl addition polymers. If the polymer contains a tertiary nitrogen which can be quaternized by the modifying agent, the use of such agents usually results in that the polymer is rendered cationic. Alternatively, the polymer to be subjected to aromatic modification can be cationic, for example a cationic vinyl addition polymer.

10 Usually the charge density of the cationic organic polymer is within the range of from 0.1 to 6.0 meqv/g of dry polymer, suitably from 0.2 to 4.0 and preferably from 0.5 to 3.0. The weight average molecular weight of synthetic main polymers is usually at least about 500,000, suitably above about 1,000,000 and preferably above about 2,000,000. The upper limit is not critical; it can be about 50,000,000, usually 30,000,000 and suitably 25,000,000.

15 The cationic organic synthetic polymer can be in any state such as, for example, in solid form, e.g. powders, in liquid form, e.g. solutions, emulsions, dispersions, including salt dispersions, etc. Examples of suitable main polymers for use as the synthetic polymer include those described in U.S. Patent Nos. 5,169,540; 5,708,071; and European Patent Applications 183,466; 525,751 and 805,234; the disclosures of which are hereby incorporated herein by reference.

20 The cationic or amphoteric polysaccharide and/or the cationic organic synthetic polymer can be present in the dispersion in amounts varying within wide limits depending on, inter alia, the molecular weight of the compounds, the degree of ionic substitution of the compounds, i.e. the charge density, the desired overall charge of the dispersion and the hydrophobic material used. Both the cationic or amphoteric polysaccharide and the cationic organic polymer can be present in an amount of up to 100% by weight, suitably from 0.1 to 35% by weight and preferably from 1 to 30% by weight, based on the hydrophobic material.

25 The dispersions according to the present invention can be anionic or cationic depending on the amount of cationic or amphoteric polysaccharides and/or cationic organic polymers and/or further additives such as dispersing/stabilising agents and protecting compounds contained in the dispersions. By anionic or cationic dispersions is understood that the dispersant is anionic or cationic, i.e. has an overall anionic or cationic charge. The dispersant (system) refers to any compounds present in the dispersion which facilitate the formation of a dispersion/emulsion such as charged polymers (polyelectrolytes) and surfactants. Suitable additives can be any dispersing/stabilising agents and protecting agent known in the art such as non-ionic polymers; cationic, anionic and amphoteric polymers derived from natural sources, i.e. polysaccharides like starch, guar gum, cellulose, chitins,

chitosans, glycans, galactans, glucans, xanthan gums, mannans, dextrans, etc., and synthetic organic polymers like condensation products, e.g. anionic polyurethanes and polymeric anionic compounds based on naphthalene, e.g. condensated naphthalene sulfonates, and further vinyl addition polymers formed from monomers with anionic groups, e.g. acrylic acid, methacrylic acid, maleic acid, itaconic acid, crotonic acid, vinylsulfonic acid, sulfonated styrene and phosphates of hydroxyalkyl acrylates and methacrylates, optionally copolymerized with non-ionic monomers including acrylamide, alkyl acrylates, styrene and acrylonitrile as well as derivatives of such monomers, vinyl esters, and the like.

Suitably, the dispersion comprises cellulose-reactive sizing agents having a sizing agent contents of from about 0.1 to about 50% by weight, suitably above 20% by weight. Dispersions containing a ketene dimer sizing agent according to the invention may have ketene dimer contents within the range of from 5 to 50% by weight and preferably from about 10 to about 35% by weight. Dispersions, or emulsions, containing an acid anhydride sizing agent according to the invention may have acid anhydride contents within the range of from about 0.1 to about 30% by weight and usually from about 1 to about 20% by weight. Dispersions of non-cellulose-reactive sizing agents generally can have sizing agent contents of from 5 to 50% by weight and preferably from 10 to 35% by weight.

By the "term" dispersion" is meant both dispersion and emulsion depending on the physical state of the sizing agent.

The dispersions according to the invention can be prepared by a method comprising homogenising a sizing agent, suitably under pressure, in the presence of an aqueous phase and a cationic or amphoteric polysaccharide or a cationic organic polymer, preferably at a temperature where the sizing agent is liquid. The obtained aqueous emulsion, which contains droplets of the sizing agent, normally having a size of from 0.1 to 3.5 μm in diameter, is then cooled. Suitable temperatures for ketene dimer sizing agents are from about 55°C to 95°C whereas lower temperatures can be employed for acid anhydrides.

The dispersions of the present invention can be used as sizing agents in conventional manner in the production of paper using any type of cellulosic fibres and it can be used both for surface sizing and internal or stock sizing. The term "paper", as used herein, is meant to include not only paper but all types of cellulose-based products in sheet and web form, including, for example, board and paperboard. The stock contains cellulosic fibres, optionally in combination with mineral fillers, and usually the content of cellulosic fibres is at least 50% by weight, based on dry stock. Examples of mineral fillers of conventional types include kaolin, china clay, titanium dioxide, gypsum, talc and natural and synthetic calcium carbonates such as chalk, ground marble and precipitated calcium carbonate.

The amount of sizing agent added to the stock can be from 0.01 to 5% by weight suitably from 0.05 to 1.0% by weight, based on the dry weight of cellulosic fibres and optional fillers, where the dosage is mainly dependent on the quality of the pulp or paper to be sized, the sizing agent used and the level of sizing desired.

5 Furthermore, the dispersions of the present invention are preferably used in the manufacture of paper from a stock containing cellulosic fibers, and optional fillers, having a high conductivity. Usually, the conductivity of the stock is at least 0.20 mS/cm, suitably at least 0.5 mS/cm, preferably at least 3.5 mS/cm. Very good sizing results have been observed at conductivity levels above 5.0 mS/cm and even above 7.5 mS/cm. Conductivity
10 can be measured by standard equipment such as, for example a WTW LF 539 instrument supplied by Christian Berner. The values referred to above are suitably determined by measuring the conductivity of the cellulosic suspension that is fed into or present in the headbox of the paper machine or, alternatively, by measuring the conductivity of white water obtained by dewatering the suspension. High conductivity levels mean high contents of salts
15 (electrolytes), where the various salts can be based on mono-, di- and multivalent cations like alkali metals, e.g. Na^+ and K^+ , alkaline earths, e.g. Ca^{2+} and Mg^{2+} , aluminium ions, e.g. Al^{3+} , $\text{Al}(\text{OH})^{2+}$ and polyaluminium ions, and mono-, di- and multivalent anions like halides, e.g., Cl^- , sulfates, e.g. SO_4^{2-} and HSO_4^- , carbonates, e.g. CO_3^{2-} and HCO_3^- , silicates and lower organic acids. The dispersion is particularly useful in the manufacture of paper from
20 stocks having high contents of salts of di- and multivalent cations, and usually the cation content is at least 200 ppm, suitably at least 300 ppm and preferably at least 400 ppm. The salts can be derived from the cellulosic fibres and fillers used to form the stock, in particular in integrated mills where a concentrated aqueous fibre suspension from the pulp mill normally is mixed with water to form a dilute suspension suitable for paper manufacture in
25 the paper mill. The salt may also be derived from various additives introduced into the stock, from the fresh water supplied to the process, or be added deliberately, etc. Further, the content of salts is usually higher in processes where white water is extensively recirculated, which may lead to considerable accumulation of salts in the water circulating in the process.

The invention is further illustrated in the following Examples which, however, are
30 not intended to limit the same. Parts and % relate to parts by weight and % by weight, respectively, unless otherwise stated.

Example 1

The sizing performance of two cationic sizing dispersions were evaluated. A
35 sizing dispersion according to the invention (dispersion no. 1) was prepared by mixing a cationic aromatic modified starch having a DS_c with molten alkyl ketene dimer (AKD) at 70 °C, passing the mixture through a homogeniser in the presence of an aqueous

solution and then cooling the dispersion so obtained. The AKD content of the dispersion was 8.5 weight % based on total dispersion.

A further cationic sizing dispersion (dispersion no. 2) according to prior art was prepared by mixing cationic starch and lignosulphonate with molten AKD having an AKD content of 15 weight %.

The papermaking stock used contained 85% of 30:30:40 pine : birch : eucalyptus sulphate and 15 % of precipitated calcium to which CaCl_2 was added. Stock consistency was 2.5 g/l having a pH of 8.1 and a conductivity of 500 μs . The dispersions were used in conjunction with retention and dewatering system comprising the same starch as used in dispersion no. 1 and condensated naphtalene sulphonate which were added to the stock separately. The cationic aromatic modified starch was added in an amount of 5 kg/ tonne, based on dry stock and the condensated naphtalene sulphonate was added in an amount of 0.5 kg/tonne.

Table 1

Sizing dispersion	Sizing dispersion added/[kg AKD/tonne dry stock]	Cobb
no. 1	0,122	30
no. 2	0,122	42

Example 2

In this example the sizing performance of the sizing dispersions of example 1 was evaluated. The retention and dewatering system added to the stock was the same as in example 1. Furthermore, the stock was the same used in example 1, however, the conductivity of the stock was 5000 μs by the addition of CaCl_2 .

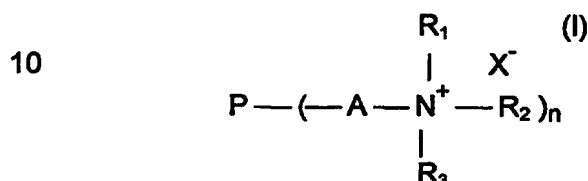
Table 2

Sizing dispersion	Sizing dispersion added/[kg AKD/tonne dry stock]	Cobb
no. 1	0,122	30
no. 2	0,122	95

1. An aqueous dispersion of a sizing agent comprising a cationic or amphoteric organic polymer, characterized in that the organic polymer comprises at least one aromatic group.

5 2. An aqueous dispersion according to claim 2, characterized in that the organic polymer is a polysaccharide or synthetic polymer.

3. An aqueous dispersion according to claim 2, characterized in that the polysaccharide has the general structural formula (I):

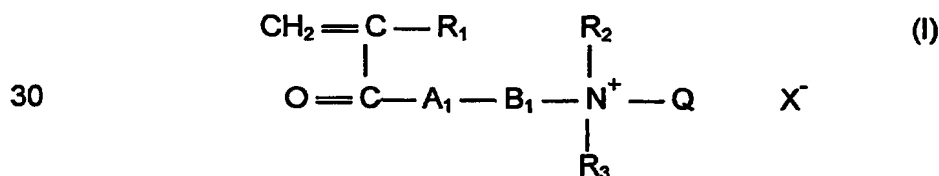


15 wherein P is a residue of a polysaccharide; A is a chain of atoms comprising C and H atoms attaching N to the polysaccharide residue, R₁ and R₂ are each H or a hydrocarbon group, R₃ is an aromatic hydrocarbon group, n is an integer from 2 up to 300000, and X⁻ is an anionic counter ion.

4. An aqueous dispersion according to claim 3, characterized in that R₁ and R₂ are alkyl groups having at least 2 carbon atoms, and R₃ is a aralkyl group including benzyl and phenylethyl groups.

5. An aqueous dispersion according to claim 2, characterized in that the synthetic polymer is a vinyl addition polymer.

6. An aqueous dispersion according to claim 5, characterized in that the vinyl addition polymer is obtained by polymerising a cationic monomer or a monomer mixture comprising a cationic monomer represented by the general formula (I):



35 wherein R₁ is H or CH₃; R₂ and R₃ are each an alkyl group having from 1 to 3 carbon atoms, A₁ is O or NH, B₁ is an alkylene group having from 2 to 8 carbon atoms or a hydroxy propylene group, Q is a substituent containing an aromatic group, and X⁻ is an anionic counterion.

7. An aqueous dispersion according to claim 6, characterized in that Q is a phenyl or a substituted phenyl group.

40 8. An aqueous dispersion according to any of the claims, characterized in that the sizing is a cellulose-reactive sizing agent.

9. Method for preparation of an aqueous dispersion by homogenising a sizing agent in the presence of an aqueous phase and a cationic or amphoteric polysaccharide or a cationic organic synthetic polymer wherein the polysaccharide and the organic synthetic polymer contains at least one aromatic group.
- 5 10. Use of an aqueous dispersion according to any of claims 1 to 9 as a stock size or surface size in the production of paper.

Abstract

The present invention refers to an aqueous dispersion of a sizing agent comprising a cationic or amphoteric organic polymer, wherein the organic polymer contains at least one aromatic group. More specifically, the organic polymers are polysaccharides or
5 synthetic polymers, the latter exemplified by vinyl addition polymers. The invention is further directed to a method for the preparation of an aqueous dispersion and to the use of the dispersion as a internal or surface size.

